

AD-A210 163

OFFICE OF NAVAL RESEARCH

Contract No. N00014-83-K-0611

R & T Code 4135003-1

Replaces old

Task No. NR 053-842

TECHNICAL REPORT NO. UK/DC/TR-24

Triazaboles and Related Triazole Derivatives of Boron

by

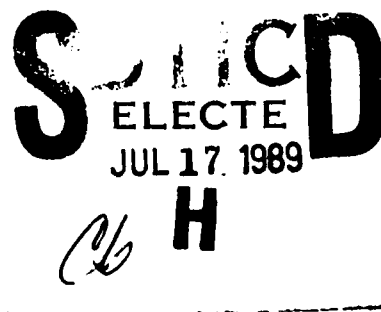
K. Niedenzu and K. R. Woodrum

Prepared for publication in

INORGANIC CHEMISTRY

University of Kentucky
Department of Chemistry
Lexington, KY 40506

July 1989



Reproduction in whole or in part is
permitted for any purpose of the United States Government

This document has been approved for public
release and sale; its distribution is unlimited

89

7

73

01

4

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION / AVAILABILITY OF REPORT prepared for publication in INORGANIC CHEMISTRY		
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UK/DC/TR-24			7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
5a. NAME OF PERFORMING ORGANIZATION Department of Chemistry University of Kentucky		6a. OFFICE SYMBOL (If applicable)	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		
5c. ADDRESS (City, State, and ZIP Code) Lexington, KY 40506-0055		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER			
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)	10. SOURCE OF FUNDING NUMBERS		
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		PROGRAM ELEMENT NO.	PROJECT NO.	XXX R&T XXX Code 4135003-1	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) TRIAZABOLES AND RELATED TRIAZOLE DERIVATIVES OF BORON (unclassified)					
12. PERSONAL AUTHOR(S) K. Niedenzu and K. R. Woodrum					
13a. TYPE OF REPORT interim technical		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) 89/7	
15. PAGE COUNT 19					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	triazaboles		
			N-triazolylboranes, tetramers,		
			N-triazolylboranes, oligomers.		
19. ABSTRACT (Continue on reverse if necessary and identify by block number)					
<p>The reaction of trimethylamine-borane, $\text{Me}_3\text{N}\cdot\text{BH}_3$, with 1,2,4-triazole (= Hst) results in the formation of an oligomer mixture of the composition $[\text{H}_2\text{B}(\text{st})]_n$; species with n up to six could be identified by mass spectrometry. Dimeric species = sym-triazaboles, $\text{R}_2\text{B}(\mu\text{-st})_2\text{BR}_2$ (2, R = hydrocarbon group), can be obtained in low yield from the condensation of R_3B with Hst, the interaction of (halo)diorganylboranes, R_2BX (X = Cl, Br) with N-trimethylsilyl-1,2,4-triazole, $\text{Me}_3\text{Si}(\text{st})$, and also by a transamination of a (dimethylamino)diorganylborane, Me_2NBR_2, with Hst. However, the major products are generally oligomeric materials $[\text{R}_2\text{B}(\text{st})]_n$. The interaction of 3-amino-1,2,4-triazole (= Hat) with excess of R_3B ultimately gives a reasonable yield of a mixture of two isomeric triazaboles of type 2 with the amino groups in either the 1,5 or 1,7 positions, whereas transamination of Me_2NBR_2 with Hat preferentially gives the 1,5-diamino isomer but in low yield. Several boron derivatives of 1,2,3-triazoles have been isolated and characterized; these include tetrameric species (derived from 1,2,3-triazole = Hut, or benzotriazole = Hbt) with a cyclic structure (6) resembling that of porphyrin, but also oligomeric materials $[\text{R}_2\text{B}(\text{ut})]_n$ and $[\text{R}_2\text{B}(\text{bt})]_n$.</p>					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kurt Niedenzu			22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL (606) 257-7073		

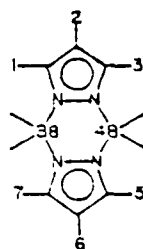
Triazaboles and Related Triazole Derivatives of Boron¹

K. Niedenzu* and K. R. Woodrum

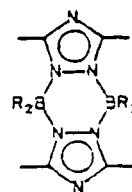
The reaction of trimethylamine-borane, $\text{Me}_3\text{N}\cdot\text{BH}_3$, with 1,2,4-triazole (= Hst) results in the formation of an oligomer mixture of the composition $[\text{H}_2\text{B}(\text{st})]_n$; species with n up to six could be identified by mass spectrometry. Dimeric species = *sym*-triazaboles, $\text{R}_2\text{B}(\mu\text{-st})_2\text{BR}_2$ (2, R = hydrocarbon group), can be obtained in low yield from the condensation of R_3B with Hst, the interaction of (halo)diorganylboranes, R_2BX (X = Cl, Br) with *N*-trimethylsilyl-1,2,4-triazole, $\text{Me}_3\text{Si}(\text{st})$, and also by a transamination of a (dimethylamino)diorganylborane, Me_2NBR_2 , with Hst. However, the major products are generally oligomeric materials $[\text{R}_2\text{B}(\text{st})]_n$. The interaction of 3-amino-1,2,4-triazole (= Hat) with excess of R_3B ultimately gives a reasonable yield of a mixture of two isomeric triazaboles of type 2 with the amino groups in either the 1,5 or 1,7 positions, whereas transamination of Me_2NBR_2 with Hat preferentially gives the 1,5-diamino isomer but in low yield. Several boron derivatives of 1,2,3-triazoles have been isolated and characterized; these include tetrameric species (derived from 1,2,3-triazole = Hut, or benzotriazole = Hbt) with a cyclic structure (6) resembling that of porphin, but also oligomeric materials $[\text{R}_2\text{B}(\text{ut})]_n$ and $[\text{R}_2\text{B}(\text{bt})]_n$.

Introduction

Although almost 100 different B- and/or C-substituted pyrazaboles (1), the neutral dimers of 1-pyrazolylboranes, are known, corresponding boron derivatives of triazoles, *i.e.*, species where two four-coordinate boron atoms are linked by two triazolyl groups, have not yet been explored. Only one



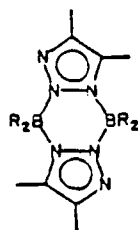
1



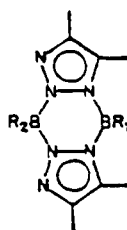
2

such compound, 4,4,8,8-tetraethyl-*sym*-triazabole (2, $R = C_2H_5$), has been described. This latter compound was obtained in moderate yield by the condensation reaction of Et_3B with 1,2,4-triazole.³ While the present work was in progress, the interaction of 3-amino-1,2,4-triazole with excess of trialkylboranes was reported to give reasonable yields of isomeric *sym*-triazaboles with NH_2 groups in either the 1,5 or 1,7 positions of 2 ($R = C_3H_7, C_4H_9$).⁴

Triazaboles derived from 1,2,3-triazoles have not yet been described. Presumably such species could exist as the isomers 3a and 3b, respectively. However, the low-temperature reaction of benzotriazole (=



3a



3b



Hbt) with Me_3B has been reported to give an unidentified complex. The latter decomposed on boiling in xylene to give an uncharacterized oligomer $[Me_2B(bt)]_n$.⁵

Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

The nitrogen atoms of the C_2N_3 rings of triazaboles (2,3) not involved in coordination to boron are potential donor sites. This feature should provide for interesting variations in the chemistry of the triazaboles as compared to that of the pyrazaboles (1). The present report describes some studies on the preparation and characterization of triazaboles and related triazole derivatives of boron.

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in $CDCl_3$ (unless otherwise noted) on a Varian VXR-400 (^{11}B , ^{15}N), XL-200 (^{11}B), or GEMINI-200 (1H , ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal Me_4Si for 1H and ^{13}C NMR, external $Et_2O \cdot BF_3$ for ^{11}B NMR, external NH_3 for ^{15}N NMR); s = singlet, d = doublet, t = triplet, q = quartet, p = quintuplet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. All ^{13}C NMR spectra were recorded in the proton decoupled mode. EI (electron impact) mass spectral data (70 eV unless otherwise noted) were obtained on a VG ZAB-2F spectrometer; data are listed to m/z 30 for 5% or more relative abundances (in parentheses) only. FD (field desorption) mass spectra were recorded on a Finnigan MAT 250 instrument, and FI (field ionization) mass spectra were recorded on a Varian MAT-CH5 instrument.

1,2,4-Triazole (= Hst; NMR data: $\delta(^1H)$ 8.60; $\delta(^{13}C)$ 147.6), 3-amino-1,2,4-triazole (= Hat; NMR data (solution in Me_2SO-d_6): $\delta(^1H)$ 12.2* (1 H, s), 7.55 (1 H, s), 5.95 (2 H, s); $\delta(^{13}C)$ 158.2, 148.1), and benzotriazole (= Hbt; NMR data: $\delta(^1H)$ 16.02 (1 H, s), 7.97 (2 H, m), 7.39 (2 H, m); $\delta(^{13}C)$ 139.0, 126.3, 115.1) were obtained from Aldrich Chemical Co., Milwaukee, WI. 1-Trimethylsilyl-1,2,4-triazole (= $Me_3Si(st)$; NMR data: $\delta(^1H)$ 8.26 (1 H, s), 8.14 (1 H, s), 0.54 (9 H, s); $\delta(^{13}C)$ 153.7, 145.9, -2.0) and *N*-trimethylsilyl-1,2,3-triazole (= $Me_3Si(ut)$ where Hut = 1,2,3-triazole; NMR data (at room temperature): $\delta(^1H)$ 7.73 (2 H, s; the signal splits at 0 °C), 0.52 (9 H, s); $\delta(^{13}C)$ 135.9, 133.0, 126.8, -1.3, -1.5; $\delta(^{15}N)$ 336.3 (s) and 269.9 (s) for the (most abundant) 2-isomer, and 372.2, 356.2, and 254.5 for the 1-isomer) were obtained from Petrarch Systems, Inc., Bristol, PA. (Bromo)dimethylborane, Me_2BBr ,

was obtained from Morton Thiokol, Inc., Alfa Products, Danvers, MA; trimethylamine-borane, $\text{Me}_3\text{N}\cdot\text{BH}_3$, and triethylborane, Et_3B , were obtained from Callery Chemical Co., Callery, PA. Diethylchloroborane, Et_2BCl ,⁶ (dimethylamino)diethylborane, Me_2NBEt_2 ,⁷ (dimethylamino)di-*n*-propylborane, $\text{Me}_2\text{NB}(\text{n-C}_3\text{H}_7)_2$,⁸ diphenylbromoborane, Ph_2BBr ,⁹ and (dimethylamino)diphenylborane, Me_2NBPh_2 ,¹⁰ were prepared by the indicated literature procedures.

N-(Trimethylsilyl)benzotriazole, $\text{Me}_3\text{Si}(\text{bt})$ (Hbt = benzotriazole), was prepared by reacting equimolar (0.25 mmol) quantities of Hbt, Et_3N , and Me_3SiCl in 150 mL of benzene (reflux for 6 h). The precipitate of $\text{Et}_3\text{N}\cdot\text{HCl}$ was filtered off and benzene was distilled off the clear filtrate (traces of unreacted benzotriazole sublimed out at this stage). The remaining product was distilled under reduced pressure to give 26.5 g (55%) of pure product, bp 125–126 °C/3 Torr.

NMR data: $\delta(^1\text{H})$ 8.05 (1 H, d, $J = 8.1$), 7.57 (1 H, d, $J = 8.3$), 7.38 (1 H, t, $J = 7.5$, of d, $J = 1.2$), 7.27 (1 H, t, $J = 6.6$, of d, $J = 1.5$), 0.61 (9 H, s); $\delta(^{15}\text{N})$ 387.1 (s), 347.0 (s), 235.0 (s). EI mass spectrum: m/z 191 (14), 148 (7), 74 (8), 73 (100), 64 (5), 63 (6), 45 (18), 43 (18), 39 (6).

$[\text{H}_2\text{B}(\text{st})]_n$ (Hst = 1,2,4-Triazole). A mixture of 3.65 g (50 mmol) of $\text{Me}_3\text{N}\cdot\text{BH}_3$, 3.45 g (50 mmol) of Hst, and 75 mL of toluene was heated to reflux for 2–4 h until one molar equivalent of hydrogen had evolved. A gummy precipitate was collected and recrystallized from 1,2-dichloroethane to give a powdery material beginning to melt near 235 °C and decomposing near 305 °C. Anal. Calcd for $[\text{C}_2\text{H}_4\text{BN}_3]_n$ ($M_r = 80.89$ for $n = 1$): C, 29.70; H, 4.98; N, 51.95. Found: C, 30.08; H, 5.07; N, 50.57.

NMR data (solution in $\text{Me}_2\text{SO}-d_6$): see text. Complete EI mass spectrum at 15 eV: m/z 485 (3), 405 (21), 404 (25), 403 (11), 324 (4), 323 (48), 322 (43), 312 (16), 320 (4), 242 (26), 241 (17), 240 (8), 174 (3), 162 (6), 161 (100), 160 (49), 159 (9), 133 (11), 132 (8), 106 (5), 105 (3), 69 (43), 42 (13), 32 (3), 31 (5). The FI mass spectrum exhibited three major peak groups in the regions m/z 404 and 323 (each ca. 70% of base peak) and 161 (base peak), and three peak groups of considerably less abundance (<10% of the base peak) in the regions m/z 484, 255, and 243. The FD mass spectrum exhibited four peak clusters centered at m/z 484, 403, 323, and 161.

$\text{Me}_2\text{B}(\mu\text{-st})_2\text{BMe}_2$ and $[\text{Me}_2\text{B}(\text{st})]_n$ (Hst = 1,2,4-Triazole). A solution of 20.1 g (166 mmol) of Me_2BBr in 100 mL of toluene was added dropwise with stirring to a solution of 23.63 g (167 mmol) of $\text{Me}_3\text{Si}(\text{tz})$ in 100 mL of toluene. An exothermic reaction occurred and the mixture was briefly refluxed. Toluene and Me_3SiBr were distilled off under reduced pressure. Part of the solid residue was sublimed off under vacuum (110 °C bath temperature at 10^{-3} Torr) and the sublimate was recrystallized from heptane to give 1.8 g of colorless product, mp 142–145 °C. Anal. Calcd for $(\text{C}_4\text{H}_8\text{BN}_3)_n$ ($M_r = 217.88$ for $n = 2$): C, 44.10; H, 7.40; N, 38.57. Found: C, 42.13; H, 7.18; N, 36.94.

NMR data: $\delta(^1\text{H})$ 8.23 (1 H, s), 0.35 (3 H, s); $\delta(^{11}\text{B})$ 0.6 (s, $h_{1/2} = 140$ Hz); $\delta(^{13}\text{C})$ 147.3, 10.4*; $\delta(^{15}\text{N})$ 248.2, 236.5. EI mass spectrum: m/z 204 (10), 203 (100), 202 (48), 201 (6), 134 (8), 94 (11), 67 (8), 66 (6), 41 (19), 40 (6). The EI mass spectrum of the sublimation residue (decomposition occurred in the range of 240–260 °C) exhibited peaks up to the region m/z 420, indicating this material to be an oligomer $[\text{Me}_2\text{B}(\text{st})]_n$ with n at least up to 4.

$\text{Et}_2\text{B}(\mu\text{-st})_2\text{BEt}_2$ and $[\text{Et}_2\text{B}(\text{st})]_n$ (Hst = 1,2,4-Triazole). Repeating the original procedure,³ variable amounts of the triazabole **2** ($\text{R} = \text{C}_2\text{H}_5$), mp 161–162 °C (lit.:³ mp 163–164 °C), were obtained but not more than about 30%.

NMR data: $\delta(^1\text{H})$ 8.25 (1 H, s), 0.78 (2 H, q, $J = 7$), 0.56 (3 H, t, $J = 7$); $\delta(^{11}\text{B})$ 2.9 (s, $h_{1/2} = 175$ Hz); $\delta(^{13}\text{C})$ 146.9, 16.1*, 8.4; $\delta(^{15}\text{N})$ 248.0, 231.2. EI mass spectrum: m/z 246 (12), 245 (100), 244 (49), 243 (6), 187 (7), 133 (5), 53 (7), 41 (26), 40 (7).

Most of the material in each preparation of the preceding $\text{Et}_2\text{B}(\mu\text{-st})_2\text{BEt}_2$ was a gummy residue. The FI mass spectrum of this product exhibited peaks indicating the presence of $[\text{Et}_2\text{B}(\text{st})]_n$ with n up to 7 but those with $n = 2$ to 4 dominated the spectrum. On prolonged heating of the material (250 °C/3 Torr) additional dimer could be sublimed off but the total yield of the triazabole never exceeded 55%.

$\text{Ph}_2\text{B}(\mu\text{-st})_2\text{BPh}_2$ and $[\text{Ph}_2\text{B}(\text{st})]_n$ (Hst = 1,2,4-Triazole) were prepared in a manner analogous to the preparation of the corresponding *B*-dimethyl derivatives via silazane cleavage (see above) using Ph_2BBr as the borane reagent. After solvent evaporation, a crude solid (melting with sintering over the range 150–250 °C) remained in essentially quantitative (97%) yield. The product was washed with water

to remove unreacted triazole and then taken up in benzene, in which most of the material dissolved readily, leaving a gummy residue. After evaporation of the benzene from the clear solution, a colorless solid remained. It melted over a wide range to give a glassy material, which decomposed near 350 °C.

NMR data: $\delta(^1\text{H})$ 7.47 (1 H, s), 7.24 (3 H, unresolved m), 6.93 (2 H, unresolved m); $\delta(^{11}\text{B})$ 2.4 ($h_{1/2}$ = 1500 Hz). A molecular ion cluster at m/z 466 was observed in the EI mass spectrum of the material to suggest $n = 2$, *i.e.*, a triazabole structure; the base peak was observed at m/z 313. The FD mass spectrum showed only the peak group for the monomer with $n = 1$ with the peaks m/z 234, 233, and 232 being observed in the correct calculated isotopic distribution for $\text{C}_{14}\text{H}_{12}\text{BN}_3$.

Thermal treatment of the above product (17 h at 250 °C/3 torr) gave a 4.5% yield of a slightly tan sublimate, most of which dissolved in CHCl_3 . After evaporation of the solvent, a colorless material of mp 252–255 °C remained. Anal. Calcd for $(\text{C}_{14}\text{H}_{12}\text{BN}_3)_n$ (M_r = 466.16 for $n = 2$): C, 72.14; H, 5.19; N, 18.03. Found: C, 71.62; H, 5.07; N, 17.67.

NMR data: $\delta(^1\text{H})$ 8.12 (1 H, s), 7.08 (3 H, m), 6.77 (2 H, d, $J = 8$, of d, $J = 2$); $\delta(^{11}\text{B})$ 2.0 (s, $h_{1/2}$ = 350 Hz); $\delta(^{13}\text{C})$ 150.5, 133.4, 128.1, 128.0. The EI mass spectrum of this material showed a small cluster in the parent ion region of the dimer (= triazabole) near m/z 466; major peaks: m/z 390 (23), 389 (100), 388 (46), 387 (6), 321 (8), 320 (33), 319 (15), 311 (5), 269 (5), 166 (27), 164 (8), 163 (8), 77 (6), 51 (6).

$\text{Et}_2\text{B}(\mu\text{-at})_2\text{BEt}_2$ (Hat = 3-Amino-1,2,4-triazole) was prepared in 66% yield as a mixture of 1,5- and 1,7-diamino isomers from excess of Et_3B and Hat following the previously reported procedure.⁴ The crude material was recrystallized from dioxane to give a product of mp 284 °C decomp. Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{B}_2\text{N}_8$ (M_r = 304.02): C, 47.41; H, 8.62; N, 36.86. Found: C, 46.38; H, 8.59; N, 33.45.

NMR data (solution in $\text{Me}_2\text{SO}-d_6$): $\delta(^1\text{H})$ 8.09 (s) + 8.02 (s) (total 1 H, ratio ca. 2:1), 6.12 (2 H, s), 0.9 to 0.2 (10 H, unresolved m); $\delta(^{11}\text{B})$ -2.6 ($h_{1/2}$ = 1500 Hz); $\delta(^{13}\text{C})$ 159.2, 146.4, 13.7*, 8.9. The isomer with the ^1H NMR signal at 8.02 ppm is slightly better soluble in hot dioxane. The EI mass spectrum exhibited the base peak at m/z 275.

$(n\text{-C}_3\text{H}_7)_2\text{B}(\mu\text{-at})_2\text{B}(n\text{-C}_3\text{H}_7)_2$ (Hat = 3-Amino-1,2,4-triazole). A mixture of 5.0 g (59 mmol) of Hat, 25.2 g (179 mmol) of $\text{Me}_2\text{NB}(n\text{-C}_3\text{H}_7)_2$, and 100 mL of toluene was refluxed with stirring for 24 h.

Toluene was distilled off under reduced pressure. The ^1H NMR spectrum of the remaining crude (liquid) product showed no (N)H signal. The material was covered with 10 mL of ethanol, 80 mL of hexane were added, and the mixture was refluxed for 1 h. The resultant precipitate was collected to give 1.7 g (16% yield) of crude material. It was recrystallized from dioxane to give a product mp 230–233 °C decomp, corresponding to the previously described 1,5-diamino-4,4,8,8-tetra-*n*-propyltriazabole.

NMR data (solution in $\text{Me}_2\text{SO}-d_6$): $\delta(^1\text{H})$ 8.07 (1 H, s), 5.09 (2 H, s), 0.9 to 0.4 (14 H, unresolved m); $\delta(^{11}\text{B})$ 1.6 (s, $h_{1/2} = 1350$ Hz). Lit.:⁴ $\delta(^1\text{H})$ (triazole region only) 8.04 (1 H, s), 6.06 (2 H, 2); $\delta(^{11}\text{B})$ 1.3 (s).

$[\text{Me}_2\text{B}(\text{ut})]_4$ (Hut = 1,2,3-Triazole).¹¹ A solution of 10.0 g (83 mmol) of Me_2BBr in 50 mL of hexane was added dropwise with stirring to a solution of 10.4 g (74 mmol) of $\text{Me}_3\text{Si}(\text{ut})$ in 50 mL of hexane. The mixture was stirred at room temperature for 3 h, the precipitate was collected, washed with pentane and dried under vacuum to give 7.4 g (97% yield) of crude slightly tan material. The latter was recrystallized from cyclohexane to give colorless crystals, mp 183 °C, in 60–70% yield. Anal. Calcd for $\text{C}_{16}\text{H}_{32}\text{B}_4\text{N}_{12}$ ($M_r = 435.76$): C, 44.10; H, 7.40; N, 38.57. Found: C, 44.04; H, 7.37; N, 37.52.

NMR data: $\delta(^1\text{H})$ 7.65 (1 H, s), 0.32 (3 H, s); $\delta(^{11}\text{B})$ 0.4 (s, $h_{1/2} = 300$ Hz); $\delta(^{13}\text{C})$ 127.3, 7.5; $\delta(^{15}\text{N})$ 359.8, 282.0. FD mass spectrum: m/z 422 (21), 421 (100), 420 (92), 419 (34), 418 (6); calcd ratio for polyisotopic $\text{C}_{15}\text{H}_{30}\text{B}_4\text{N}_{12}$ (= $[\text{Me}_2\text{B}(\text{ut})]_4$ minus CH_3): 422 (21), 421 (100), 420 (92), 419 (32), 418 (5). The EI mass spectrum exhibited a weak ion cluster at m/z 421 and a base peak at m/z 312.

$[\text{Et}_2\text{B}(\text{ut})]_4$ (Hut = 1,2,3-Triazole) was prepared in analogous fashion as the preceding compound employing Et_2BCl as borane reagent. The compound was obtained in 50% yield as colorless crystals, mp 193–195 °C (after recrystallization from cyclohexane and then heptane). Anal. Calcd for $\text{C}_{24}\text{H}_{28}\text{B}_4\text{N}_{12}$ ($M_r = 547.96$): C, 52.61; H, 8.83; B, 7.89; N, 30.67. Found: C, 52.21; H, 9.05; B, 8.15; N, 30.06.

NMR data: $\delta(^1\text{H})$ 7.62 (1 H, s), 0.87 (2 H, q, $J = 8$), 0.56 (3 H, t, $J = 8$); $\delta(^{11}\text{B})$ 2.3 ($h_{1/2} = 800$ Hz); $\delta(^{13}\text{C})$ 128.0, 12.7, 8.7; $\delta(^{15}\text{N})$ 361.4, 278.2. The EI mass spectrum (14 eV) exhibited an ion cluster at m/z 519 and a base peak at m/z 383.

$[\text{H}_2\text{B}(\text{bt})]_n$ (Hbt = Benzotriazole). A mixture of 5.0 g (42 mmol) of Hbt, 3.1 g (42 mmol) of $\text{Me}_3\text{N}\cdot\text{BH}_3$, and 150 mL of toluene was heated under reflux for 4 h. A colorless precipitate formed on cooling to room temperature. It was collected, washed with petroleum ether, and dried under vacuum to give 5.1 g (93%) of crude product, mp 262–270 °C decomp (after recrystallization from mesitylene). Anal. Calcd for $(\text{C}_6\text{H}_6\text{BN}_3)_n$ ($M_r = 261.90$ for $n = 2$): C, 55.03; H, 4.62; N, 32.09. Found: C, 55.07; H, 4.73; N, 31.34.

NMR data: $\delta(^1\text{H})$ 7.94 (2 H, m), 7.48 (2 H, m), 4.2* (2 H); $\delta(^{11}\text{B})$ -8.7 (s, $h_{1/2} = 300$ Hz); $\delta(^{13}\text{C})$ 138.7, 127.1, 114.6. The EI mass spectrum exhibited a parent ion cluster for $n = 4$ at m/z 524 and a base peak at m/z 261. In the FI mass spectrum, a base peak cluster was observed near m/z 523, a much smaller cluster (10% relative abundance) near m/z 260, and a very minor cluster (ca. 2% relative abundance) near m/z 131.

$[\text{Me}_2\text{B}(\text{bt})]_4$ (Hbt = Benzotriazole). A solution of 5.0 g (40 mmol) of Me_2BBr in 25 mL of hexane was added dropwise and with stirring to a solution of 7.3 g (38 mmol) of $\text{Me}_3\text{Si}(\text{bt})$ in 100 mL of hexane. A colorless gummy precipitate formed and the mixture was allowed to stand overnight. The solution was decanted, the residue washed with hexane and dried under vacuum to give an essentially quantitative yield (6 g) of product. For purification it was dissolved in a minimal amount of benzene, and the solution was topped with the sixfold amount of acetonitrile. On standing for several days, crystals of the compound formed which were collected and dried, mp 190–195 °C. Anal. Calcd for $\text{C}_{32}\text{H}_{40}\text{B}_4\text{N}_{12}$ ($M_r = 636.00$): C, 60.43; H, 6.37; N, 26.43. Found: C, 60.09; H, 6.37; N, 26.17.

NMR data: $\delta(^1\text{H})$ 7.61 (1 H, d, $J = 7$, of d, $J = 3$), 7.32 (1 H, d, $J = 7$, of d, $J = 3$), 0.55 (3 H, s); $\delta(^{11}\text{B})$ 1.1 (s, $h_{1/2} = 250$ Hz). The highest ion peaks observed in the EI mass spectrum of the compound were at m/z 621, corresponding for the loss of one methyl group from the parent species.

$[\text{Et}_2\text{B}(\text{bt})]_n$ (Hbt = Benzotriazole). A mixture of 6.0 g (50 mmol) of Hbt, 7 mL (50 mmol) of Et_2B , and 75 mL of xylene was refluxed for 2 h when gas evolution ceased. The colorless precipitate was collected, washed with water (to remove unreacted Hbt) and dried to give 8.2 g (88%) of crude (oligomeric) product, mp near 375 °C sintering and decomp. Anal. Calcd for $(\text{C}_{10}\text{H}_{14}\text{BN}_3)_n$ ($M_r = 374.10$ for $n = 2$): C, 64.21; H, 7.54; N, 22.46. Found: C, 64.40; H, 7.16; N, 22.09.

No solvent for recording NMR spectra was found. EI mass spectrum (15 eV): m/z 187 (7), 159 (9), 158 (79), 157 (18), 131 (11), 130 (79), 129 (21), 120 (13), 119 (100), 116 (10), 103 (5), 102 (11), 92 (6), 91 (74), 65 (5), 64 (26), 52 (6), 45 (35), 44 (32), 41 (10). The FD mass spectrum of the material exhibited an ion cluster in the region of the monomer only. No breakdown to yield a defined dimer or tetramer was found to occur on thermal treatment of the material.

Alternate Procedure. A mixture of 8.0 g (67 mmol) of Hbt, 5.0 g (44 mmol) of Me_2NBEt_2 , and 200 mL of toluene was refluxed for 4 h. After cooling to room temperature, a colorless precipitate (2.0 g, 24%) of material, identical (mass spectrum) with that of the preceding experiment, was collected.

Alternate Procedure. A solution of 8 g (80 mmol) of Et_2BCl in 20 mL of hexane was added dropwise to a solution of 13 g (68 mmol) of $\text{Me}_3\text{Si}(\text{bt})$ in 60 mL of hexane. The mixture was stirred at room temperature for 30 min and the precipitate was collected, washed with hexane, and dried to give 13 g (essentially quantitative yield) of product, mp 385 °C sintering and decomp. EI mass spectrum (15 eV): m/z 345 (2), 344 (2), 187 (14), 186 (5), 159 (12), 158 (98), 157 (26), 148 (5), 147 (21), 131 (13), 130 (100), 129 (29), 119 (29), 116 (14), 103 (11), 102 (11), 91 (30), 69 (6), 64 (9), 57 (6).

$[(n\text{-C}_3\text{H}_7)_2\text{B}(\text{bt})]_n$ (Hbt = Benzotriazole). A mixture of 8.0 g (67 mmol) of Hbt, 5.0 g (35 mmol) of $\text{Me}_2\text{NB}(n\text{-C}_3\text{H}_7)$, and 200 mL of toluene was refluxed for 6 h. The clear solution was kept overnight and the resultant precipitate was collected to give 2.4 g (32%) of crude product. It was recrystallized from toluene to give a material of mp 215–225 °C decomp. Anal. Calcd for $(\text{C}_{12}\text{H}_{18}\text{BN}_3)_n$ ($M_r = 430.22$ for $n = 2$): C, 67.00; H, 8.43; N, 19.53. Found: C, 67.23; H, 8.61; N, 20.26.

NMR data: $\delta(^1\text{H})$ 7.60 (1 H, unresolved), 7.33 (1 H, d, $J = 6$, of d, $J = 3$), 1.17 (2 H, t, $J = 7$), 0.75 (5 H, m); $\delta(^{11}\text{B})$ -0.3 (s, $h_{1/2} = 1150$ Hz); $\delta(^{13}\text{C})$ 138.7, 126.1, 116.1, 36.0, 18.8, 18.0. EI mass spectrum (14 eV): m/z 215 (8), 173 (11), 172 (100), 171 (26), 144 (63), 143 (18), 142 (5), 119 (22), 116 (70), 102 (12), 91 (13), 71 (10), 32 (8). The highest ion cluster seen in the 70 eV EI mass spectrum of the compound was observed near m/z 817, indicating a loss of one alkyl group from the tetramer; the base peak was observed at m/z 172. The FD mass spectrum showed only peaks in the regions m/z 817, 387, and 215.

Solvent was stripped off the filtrate of the above experiment to give 1.5 g of a gummy residue. The FI mass spectrum of this material showed peaks in the regions m/z 387 and 239 only.

Results

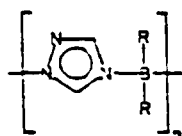
Boron Derivatives of 1,2,4-Triazole (= Hst). The preparation of the parent compound of the *sym*-triazabole system, *i.e.*, **2** with $R = H$, was attempted in analogy to the preparation of pyrazabole by condensation of $Me_3N \cdot BH_3$ with 1,2,4-triazole (= Hst). The reaction resulted in the formation of an oligomeric product and no individual species could be separated. The highest ion cluster (of low abundance) in the (15 eV) EI mass spectrum of the product was observed in the region near m/z 485 indicating the presence of up to a hexameric material, *i.e.*, $[H_2B(st)]_6$. The FI mass spectrum exhibited several peak groups (see experimental data) to support the assumption that an oligomer mixture was obtained. Such a mixture was also indicated by the ^{11}B NMR spectrum of the material, which exhibited a broad (approximately 2500 Hz) signal centered near -5 ppm, suggesting the formation of a number of species with different though similar ^{11}B chemical shifts. In addition, the 1H NMR spectrum of the material exhibited five singlets at 9.25, 9.22, 8.59, 8.54, and 8.42 ppm in approximately 2:2:1:2:1 ratio, and several additional but considerably smaller signals for the triazolyl protons, and also a very broad (B)H resonance signal at 3 to 4 ppm.

The fragmentation pattern of the EI mass spectrum of the material was noticeably different from that observed for pyrazabole, $H_2B(\mu-pz)_2BH_2$.¹² peak clusters corresponding to m/z values for $([H_2B(st)]_n + BH_2)$, for example in the region m/z 175 corresponding to a species with $n = 2$ plus BH_2 , were consistently observed. This suggests the possibility that all three nitrogen atoms of individual triazolyl groups may participate in the oligomer formation.

The reaction of Me_2BBr with (fluxional) *N*-trimethylsilyl-1,2,4-triazole, $Me_3Si(st)$, which was studied at various temperatures ranging from 0 to 80 °C, gave only a small amount of the desired *sym*-triazabole **2** with $R = CH_3$; the bulk of the product was again what appears to be an oligomer mixture. Similarly, the transamination of Me_2NBPh_2 with Hst resulted primarily in a mixture of oligomers.

On repeating of the original³ condensation of Et₃B with Hst, only a small amount of the triazabole 2 (R = C₂H₅) was obtained. Even when the reactions were performed under seemingly identical conditions, the product yields varied considerably but never exceeded 30%; most of the product was a gummy mixture of oligomers as supported by the mass spectral data; however, the latter also seemed to indicate a slow conversion of oligomer to the corresponding triazabole (2) on heating of the material under vacuum. Indeed, when the cited gummy material was treated at temperatures near 250 °C/3 Torr, a substantial amount (up to 25%) of additional triazabole 2 (R = C₂H₅) sublimed off over a period of 24 h.

All of the data suggest that the primary coordination of individual N-triazolylborane units does not involve vicinal nitrogen atoms as in the triazabole structure 2 but that 4 is likely to be the better



4

illustration for the oligomer, and that, at least initially, the formation of the latter seems to predominate over that of a triazabole (2).

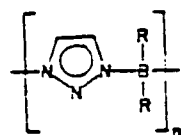
Similarly, although a small amount of the pure triazabole Ph₂B(μ-st)₂BPh₂ could be isolated and characterized, most of the material was oligomeric. The FD mass spectrum of the latter gave peaks only for the monomeric species Ph₂B(st). This observation may suggest that the oligomer is a linear material.

Derivatives of 3-Amino-1,2,4-triazole (= Hat). The yield of an isolable *sym*-triazabole of type 2 is considerably increased by reaction of an excess of a trialkylborane with Hat. However, in this case isomeric species with the NH₂ groups in either the 1,5 or 1,7 positions were obtained. Usually, one of the isomers can be isolated in the pure state.

Replacement of the R₃B by Me₂NBR₂ in the reaction with Hat gave a considerably lower yield of 2 but led preferentially to the 1,5-diamino isomer.

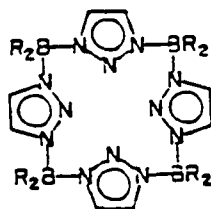
It should be emphasized that in the reactions using Hat both the annular NH and the terminal NH₂ groups are borylated to form species of the type R₂B[μ-N₃C₂H(NHBR₂)₂]₂BR or even R₂B[μ-N₃C₂H{N(BR₂)₂}]₂BR₂ as intermediates. (No effort was made to characterize these species; they are, however, readily recognized by the observation of three-coordinate boron at 33.3 ppm in the ¹¹B NMR spectra of such intermediates.) The NH₂ group is then restored during the work-up via an alcoholysis to give the final product.

Derivatives of 1,2,3-Triazole (= Hut). N-Borylated 1,2,3-triazoles were prepared by reaction of 2-trimethylsilyl-1,2,3-triazole, Me₃Si(ut), with (halo)diorganylborananes, R₂BX (X = Br, Cl). (Note: Me₃Si(ut) is fluxional; see Experimental Section.) The transient monomeric species R₂B(ut) do not seem to exhibit a tendency to dimerize with the formation of triazaboles of type 3. Rather, oligomeric species



5

of type 5 appear to be the preferred products. These may be linear and/or cyclic, but for R = CH₃ the cyclic species 5 with n = 4, i.e., 6, was found to be the exclusive product. Only one single resonance line



6

was observed for the triazole rings in both the ¹H and ¹³C NMR spectra of [Me₂B(uz)]₄ and the mass spectral data of the product clearly established the tetrameric nature of the species. The highest peak

group observed in the EI spectrum (near m/z 421) was that for an ion where loss of a methyl group from the molecular ion M^+ of the tetramer had occurred, and the base peak of the spectrum (m/z 312) corresponded to a loss of a methyl group plus a $\text{Me}_2\text{B}(\text{ut})$ unit from M . In addition, ions of relatively high abundances were observed for compositions corresponding to $\text{Me}_6\text{B}_3(\text{ut})_2$ (m/z 259), $\text{Me}_3\text{B}_2(\text{ut})_2$ (m/z 203), and $\text{Me}_4\text{B}_2(\text{ut})$ (m/z 150). The FD mass spectrum of the species exhibited only a cluster in the m/z 421 region. These data clearly support the structure 6, which resembles that of porphin and was confirmed by an X-ray crystal structure analysis.¹¹

The B-diethyl derivative of 1,2,3-triazole was also obtained as the tetramer (6); there were no indications for the formation of a triazabole of type 3 nor for that of other oligomeric materials.

Derivatives of Benzotriazole (= Hbt). The reaction of $\text{Me}_3\text{N}\cdot\text{BH}_3$ with Hbt gave what appeared to be primarily the tetramer $[\text{H}_2\text{B}(\text{bt})]_4$ with a cyclic structure analogous to 6. However, the FI mass spectral data suggest the additional presence of a small amount of a dimer and traces of a monomer. It may well be that under the reaction conditions the tetramer of type 6 is the dominant product, but that some dimer and (linear?) oligomer are also formed. This conclusion is also borne out by the relative wide melting range of the product.

Reaction of Me_2BBr with $\text{Me}_3\text{Si}(\text{bt})$ initially gave a gummy material, $[\text{Me}_2\text{B}(\text{bt})]_n$, which was obviously oligomeric in nature. Slow crystallization gave a sharp melting product, the ^1H NMR spectrum of which exhibited only two sharp signals in the aromatic region. In conjunction with the mass spectral data, the crystalline material is the tetramer corresponding to 6 (see also below).

Similarly, the reaction of Hbt with $\text{Me}_2\text{NB}(\text{n-C}_3\text{H}_7)_2$ proceeded to give what appeared to be the tetramer $[(\text{C}_3\text{H}_7)_2\text{B}(\text{bt})]_4$ since the highest peak seen in the 70 eV EI mass spectrum of the resultant product was observed at m/z 817. In the 14 eV spectrum, the highest peak was observed at m/z 215 (M^+ for a dimer) with a base peak at m/z 170. This would indicate the ready loss of a propyl group from the parent ion M^+ of a triazabole of type 3. (This fragmentation is analogous to that of B-tetraorganylpirazaboles, $\text{R}_2\text{B}(\mu\text{-pz})_2\text{BR}_2$, which is generally dominated by a lack of a molecular ion and features the parent ion M^+ minus one organyl group as the highest ion that can be observed.¹³) On

the other hand, the FD mass spectrum of the species showed a peak cluster in the region m/z 817, corresponding to a species $[R_2B(bt)]_4$ with $n = 4$ minus 43 ($= C_3H_7$), as well as peaks near m/z 387 and 215. Another interesting feature was the observation of only two 1H NMR signals for the C_6H_4 group of the species and also the equivalence of the C(1) and C(2) as well as C(3)/C(6) and C(4)/C(5) atoms of the benzene ring in the ^{13}C NMR spectrum. This cannot be in consonance with a triazabole structure 3 but clearly suggests a symmetrical structure where N(1) and N(3) of the five-membered C_2N_3 ring are involved in bonding to boron. These data seem to be best interpreted by assuming that the tetramer is formed as the primary product but is contaminated by additional oligomers.

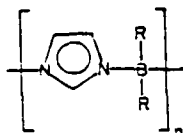
Surprisingly, the EI and FD mass spectral data of $[Et_2B(bt)]_n$ obtained from either Et_3B and Hbt or Me_2NBEt_2 and Hbt exhibited only one ion cluster near m/z 187 suggesting it to be a monomer. A small amount of the dimer was seen in the EI mass spectrum of the product obtained from the reaction of Et_2BCl with $Me_3Si(bt)$. Since the effect of a BEt_2 versus those of a $B(C_3H_7)_2$ group on the degree of oligomerization should be negligible, it may well be that the method of preparation affects the value of n .

Discussion

When pyrazole ($= Hpz$) or C-substituted derivatives thereof ($= Hpz^*$) are condensed with a trigonal borane (or a Lewis base adduct thereof), pyrazaboles of 1 are readily obtained.² However, reactions involving 3-monosubstituted pyrazoles lead to the formation of isomers, *i.e.*, mixtures of the 1,5- and 1,7-disubstituted pyrazaboles are obtained.¹⁴⁻¹⁶ This illustrates the fluxionality of the assumed intermediate monomeric (1-pyrazolyl)borane, $R_2B(pz^*)$ (containing trigonal boron), a feature which has been well established.^{15,17-19}

The reaction of 1,2,4-triazole ($= Hst$) with a trigonal borane to yield a *sym*-triazabole (2) should pose no problem were it not for the fact that the third annular nitrogen can also serve as a binding site to boron. Thus, an intermediate monomeric N-triazolylborane, $R_2B(st)$, may either utilize vicinal nitrogen atoms of the triazole ring to dimerize and yield a triazabole (2), or coordinative saturation of the boron may occur by linking of the N(1) and N(4') atoms of two triazole rings, rendering the formation of a dimer to be unlikely. Rather, this latter situation is similar to that of boron derivatives of imidazole ($= Hiz$) where the

few known monomeric species, $R_2B(iz)$, have also been found to be fluxional undergoing a 1,3-shift of the N-bonded boryl group.¹⁸ However, if the boron substituents are not strongly electron-donating,



7

association occurs to give oligomeric $[R_2B(iz)]_n$ species of type 7 containing four-coordinate boron.²⁰⁻²³ Although the tetrameric species with $n = 4$ and presumably cyclic structure appear to be predominate,^{22,23} higher molecular weight chain-type oligomers with $n = 40$ to 80 have been reported.²⁰ On the other hand, if C(2) is substituted, *e.g.*, using 2-methylimidazole, reaction with a trigonal borane provides a (presumably cyclic) tetramer in essentially quantitative yield.²⁰

In the case of a N-borylated 1,2,4-triazole species there is no obvious reason why a pyrazabole-type dimerization should be favored over an oligomerization typical for imidazolylboranes. Presumably, both processes compete although the present results suggest that oligomerization (to yield 4) is favored over dimerization (to yield 2). This observation can be interpreted by assuming that after attachment of boron to N(1) of Hst, N(2) and N(4) are of about equal basicity and coordinative saturation of the boron could lead to the formation of both 2 and oligomers 4. The fluxionality (= migration of the BR_2 group among the various nitrogen sites) of the assumed monomeric intermediate $R_2B(st)$ may also favor the formation of both types of species. Since prolonged thermal treatment of the initial product gave increased yields of 2, the latter generally appears to be the thermodynamically favored product.

This situation is different when 3-amino-1,2,4-triazole is employed. It is likely that in this case the fluxionality of the presumed monomeric intermediate is impaired by the substitution at C(3) of the triazole ring, thus forcing dimerization rather than oligomerization.

The oligomerization involving N(1) and N(3) as binding sites for boron is clearly preferred in the case of boron derivatives of 1,2,3-triazoles and the formation of tetrameric species (6) seems to predominate. This observation supports the assumption that, as a rule, non-neighboring nitrogen atoms generally are the preferred binding sites for the coordinative saturation of boron of N-borylated 1,2,3-triazole monomers rather than formation of a N(1)-B-N(2') arrangement. These results suggest that monomeric N-borylated triazoles behave more similar in their intermolecular coordinative behavior to the corresponding imidazole rather than pyrazole derivatives.

Acknowledgment. This work was supported by the Office of Naval Research (K.N.). FI and FD mass spectra were obtained through the courtesy of Prof. A. Meller and Dr. D. Böhler, Georg August University, Göttingen, Federal Republic of Germany.

References

- (1) Boron-Nitrogen Compounds. 121. Part 120: Mariategui, J. F.; Niedenzu, K. *J. Organomet. Chem.*, in press.
- (2) Niedenzu, K.; Trofimenko, S. *Top. Curr. Chem.* **1986**, *131*, 1-37.
- (3) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3165-3170.
- (4) Dorokhov, V. A.; Amachyan, A. R.; Bochkareva, M. N.; Teslya, I. A.; Starikova, Z. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1987**, *36*, 147-151.
- (5) Garnovskii, A. D.; Okhlobystin, O. Yu.; Osipov, O. A.; Yunusov, K. M.; Kolodyazhnyi, Yu. V.; Golubinskaya, L. M. *J. Gen. Chem. USSR* **1972**, *42*, 910-914.
- (6) Köster, R.; Grassberger, M. A. *Liebigs Ann. Chem.* **1968**, *719*, 169-186.
- (7) Alam, F.; Niedenzu, K. *Inorg. Synth.* **1983**, *22*, 209-211.
- (8) Emerick, D. P.; Komorowski, L.; Lipinski, J.; Nahm, F. C.; Niedenzu, K. *Z. Anorg. Allg. Chem.* **1980**, *468*, 44-54.
- (9) Nöth, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1968**, *11*, 399-405.
- (10) Niedenzu, K.; Beyer, H.; Dawson, J. W. *Inorg. Chem.* **1962**, *1*, 738-742.

- (11) The crystal and molecular structure of this tetramer has been determined by single-crystal x-ray diffraction. The results will be published elsewhere in conjunction with other data.
- (12) May, C. E.; Niedenzu, K.; Trofimenko, S. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* 1976, 31B, 1662-1666.
- (13) May, C. E.; Niedenzu, K.; Trofimenko, S. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* 1978, 33B, 220-223.
- (14) Petersen, L. K.; Thé, K. I. *Can. J. Chem.* 1979, 57, 2520-2522.
- (15) Alam, F.; Niedenzu, K. *J. Organomet. Chem.* 1983, 243, 19-30.
- (16) Niedenzu, K.; Niedenzu, P. M.; Warner, K. R. *Inorg. Chem.* 1985, 24, 1604-1606.
- (17) Niedenzu, K.; Weber, W. *J. Organomet. Chem.* 1980, 195, 25-28.
- (18) Weber, W.; Niedenzu, K. *J. Organomet. Chem.* 1981, 205, 147-156.
- (19) Alam, F.; Niedenzu, K. *J. Organomet. Chem.* 1982, 240, 107-119.
- (20) Trofimenko, S. *J. Am. Chem. Soc.* 1967, 89, 3903-3904.
- (21) Boenig, I. A.; Conway, W. R.; Niedenzu, K. *Synth. React. Inorg. Met.-Org. Chem.* 1975, 5, 1-5.
- (22) Breakall, K. R.; Rendle, D. F.; Storr, A.; Trotter, J. *J. Chem. Soc. Dalton Trans.* 1975, 1584-1589.
- (23) Müller, K.-D.; Komorowski, L.; Niedenzu, K. *Synth. React. Inorg. Met.-Org. Chem.* 1978, 8, 149-155.

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3	Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1	Chief of Naval Research Special Assistant for Marine Corps Matters Code 00MC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1	Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 <u>high quality</u>	Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1	David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1		

ORGANOELEMENT CHEMISTRY - Distribution List

Professor O. T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214
R&T Code 4135002

Professor Herbert C. Brown
Purdue University
Department of Chemistry
West Lafayette, IN 47907
R&T Code 4135011

Professor Steven L Buchwald
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139
R&T Code 4135014

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514
R&T Code 4135007

Professor M. Frederick Hawthorne
Department of Chemistry
405 Hilgard Avenue
University of California
Los Angeles, CA 90024
R&T Code 4135004

Professor Robert H. Neilson
Department of Chemistry
Texas Christian University
Fort Worth, TX 76843
R&T Code 4135005

Professor Kurt Niedenzu
Department of Chemistry
University of Kentucky
Lexington, KY 40506
R&T Code 4135003

Professor Richard L. Wells
Department of Chemistry
Duke University
Durham, NC 27706
R&T Code 4135008